John von Neumann Institute for Computing

Theoretical Studies on the Higher Oxidation States of Iron

M. Atanasov

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 2, ISBN 3-00-005746-3, p. 3, 2000.

http://www.fz-juelich.de/nic-series/

Theoretical Studies on the Higher Oxidation States of Iron

M.Atanasov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Bl.11,1113 Sofia, Bulgaria and Fachbereich Chemie und Zentrum für Materialwissenschaften der Philipps-Universität, Hans-Meerweinstr.1, D-35043 Marburg, Germany*

Abstract

The stabilisation of the high oxidation states of the 3d transition metals (TM) is an important problem in inorganic chemistry. Examples are the high-T_c Cu^{III} oxides and the materials for energy storage, such as the rechargeable Li batteries based on oxides of Ni^{III}/Ni^{IV}, Co^{III}/Co^{IV} and Mn^{III}/ Mn^{IV}. In this contribution we report density functional (DFT) and multiconfiguration self consistent field (MCSCF) calculations on the oxo FeO_4^{2-} (Fe^{VI}) and the hypothetical oxo FeO_4^{-} (Fe^{VII}), FeO_4 (Fe^{VIII}) and peroxo $FeO_2(O\text{-}O)^{z}$ [z=-2(Fe^{IV}),z=-1(Fe^{V}), z=0(Fe^{VI})]; $Fe(O\text{-}O)_2^{z}$ [z=-2(Fe^{II}), z=-1(Fe^{III}), z=0(Fe^{IV})] and $FeO(O\text{-}O)_2^{z}$ [z=-2(Fe^{IV}),z=-1(Fe^{V}), z=0(Fe^{VI})] clusters. The results show the potential of stabilising Fe^{VII} and Fe^{VIII} in tetrahedral oxo coordination. On the basis of absolute electronegativities calculated using DFT, it is predicted, that FeO_4 will be rather oxidising even stronger than Cl_2 and O_2. Based on a comparison between total bonding energies of $M_1M_2Fe^{VI}O_4$ (M_1,M_2=Li, K), $MFe^{VII}O_4$ (M=Li,K) and $Fe^{VI}O_4$ clusters, possible synthetic routes for electrochemical preparation of FeO_4^{-} and FeO_4 species are discussed.

It is demonstrated that the DFT method is very powerful in calculating and predicting not only ground state but also excited state electronic structures and their properties in compounds with transition metals in their high oxidation states. Such compounds are sometimes not well characterised or at least they are synthetic targets in view of their promissing properties for energy storage and energy conversion.

* adress for correspondence; E-mail: ata@ax1505.chemie.uni-marburg.de